

金鱼藻的化学成分*

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摘要: 从金鱼藻 (*Ceratophyllum demersum* L.) 全草的乙醇提取物中分离鉴定了其中 7 个, 分别为: 苜蓿素-7-*O*- β -D-葡萄糖苷 (1), naringenin-7-*O*- β -D-葡萄糖苷 (2), 七叶内酯 (3), β -谷甾醇 (4), 7-羟基- β -谷甾醇 (5), 7-甲氧基- β -谷甾醇 (6), 十六碳脂肪酸 (7)。化合物 (3) 为首次从金鱼藻中分离得到。

关键词: 金鱼藻; 苜蓿素-7-*O*- β -D-葡萄糖苷; Naringenin-7-*O*- β -D-葡萄糖苷; 七叶内酯

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Chemical Constituents from *Ceratophyllum demersum* (Ceratophyllaceae)

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Abstract: In this paper, we represent seven compounds [tricin-7-*O*- β -D-glucoside (1), naringenin-7-*O*- β -D-glucoside (2), esculetin (3), β -sitosterol (4), 7-hydroxyl- β -sitosterol (5), 7-methoxyl- β -sitosterol (6) and palmitic acid (7)]. All compounds were isolated from *Ceratophyllum demersum* L. which was collected from Lijiang. We compare them with compounds isolated from the material collected from Kunming by TLC. The results show that the types of main secondary metabolite in *Ceratophyllum demersum* L. in Yunnan are similar.

Key words: *Ceratophyllum demersum*; Tricin-7-*O*- β -D-glucoside; Naringenin-7-*O*- β -D-glucoside; Esculetin

Ceratophyllum demersum L. (Ceratophyllaceae), is a kind of perennial hydrophyte plant and widely distributed throughout ponds and rivers in China. Usually it was used as goldfish feed, as well as folk medicine for the treatments of internal injury and haematemesis (Wu *et al.* 2003). Foreign scholars have already isolated two compounds of flavonoid and seven kinds of Phytosterol (Bankova *et al.* 1995); however, the chemical constituents of *Ceratophyllum demersum* L. from China have not been analysed. We try to systematically study on chemical constituents of the plants and provide accessory evidence to determine the systematical position of Ceratophyllaceae. In the paper, the

chemical structures of seven compounds from above mentioned plant would be reported.

Experimental

General Melting points were measured on a WC-1 micro melting points apparatus and are uncorrected. ¹H NMR, ¹³C NMR and 2D-NMR spectra were recorded on a Bruker AM-400 MHz and a DRX-500 spectrometer with TMS as internal standard. FAB-MS: Autospec-3000 spectrometer (in *m/z*); Silica gel (200-300 mesh) was produced by Qingdao Marine Chemical Company. Rp-18 (40-60 μ , Merck). Sephadex LH-20 (Amersham Pharmacia Biotech AB).

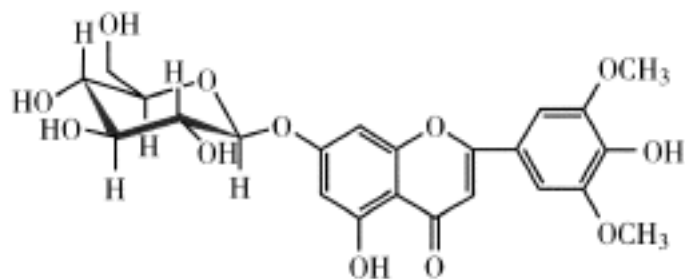
Plant Material The *Ceratophyllum demersum* L. was collected in Lijiang, Yunnan Province, P. R. C. in May 2005.

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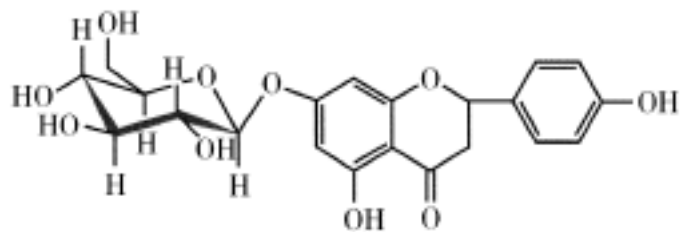
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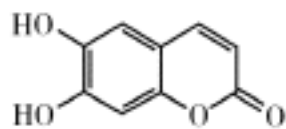
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The plant material was identified by Dr. Li Xiaoxian (Kunming Institute of Botany, the Chinese Academy of Sciences), and a voucher specimen was deposited at the Laboratory of Phytochemistry, Kunming Institute of Botany.

Extraction and Isolation Dried chipped *Ceratophyllum demersum* L. (5 kg) was extracted with EtOH. The extract was filtered, concentrated *in vacuo* to a suitable volume, suspended in water, and then successively partitioned with Petroleum Ether, CHCl_3 , and EtOAc, respectively. These three extracts were respectively concentrated *in vacuo* to afford residues of Petroleum Ether (62 g), residues of CHCl_3 (25 g) and residues of EtOAc (11 g).

The EtOAc portion was subjected repeatedly to silica gel chromatography and stepwisely eluted with CHCl_3 - Me_2CO (from CHCl_3 to CHCl_3 - Me_2CO 1:1) to yield tricetin-7-O-D-glucoside (**1**) (10 mg), Naringenin-7-O-D-glucoside (**2**) (7 mg) and esculetin (**3**) (7 mg), respectively.

The CHCl_3 portion was subjected repeatedly to silica gel chromatography and stepwisely eluted with CHCl_3 - Me_2CO (from CHCl_3 to CHCl_3 - Me_2CO 1:1) to yield β -sitosterol (**4**) (10 mg), 7-hydroxyl- β -sitosterol (**5**) (9 mg), 7-methoxyl- β -sitosterol (**6**) (7 mg), palmitic acid (**7**) (12 mg), respectively.

Structural Identification

Tricin-7-O-D-glucoside (**1**), $\text{C}_{23}\text{H}_{24}\text{O}_{12}$, yellow powder. mp 260.5–261 (MeOH). ^1H NMR (400 MHz, DMSO): 6.44 (1H, s, H-3), 6.95 (1H, s, H-6), 7.04 (1H, s, H-8), 7.34 (2H, s, H-2, 6), 3.87 (6H, s, OMe), 4.69 (1H, d, H-1), 3.72–3.15 (6H, m, H-2, 3, 4, 5, 6). ^{13}C NMR (125 MHz, DMSO): 164.3 (C-2), 103.8 (C-3), 182.1 (C-4), 161.1 (C-5), 99.6 (C-6), 163.1 (C-7), 95.4 (C-8), 105.5 (C-9), 157.0

(C-10), 120.3 (C-1), 104.6 (C-2, 6), 148.3 (C-3, 5), 140.2 (C-4), 100.2 (C-1), 73.2 (C-2), 76.5 (C-3), 69.8 (C-4), 77.4 (C-5), 60.8 (C-6), 56.5 (3, 5-OMe). (Ramachander G. *et al.* 1978).

Naringenin-7-O-D-glucoside (**2**), $\text{C}_{21}\text{H}_{22}\text{O}_{10}$, mp 225. ^1H NMR (400 MHz, CD_3OD): 2.72 (1H, H-3, d, $J=12.3$ Hz), 3.13 (1H, H-3, d, $J=12.3$ Hz), 3.15–3.50 (4H, m, H-2, 3, 4, 5), 3.62 (1H, H-6, d, $J=11.9$ Hz), 3.70 (1H, H-6, d, $J=11.9$ Hz), 5.40 (1H, H-2, brs), 6.18 (1H, H-8, s), 6.20 (1H, H-6, s), 4.96 (1H, H-1, d, $J=4.3$ Hz), 6.80 (2H, H-3 and H-5, d, $J=7.5$ Hz), 7.31 (2H, H-2 and H-4, d, $J=7.5$ Hz); ^{13}C NMR (125 MHz, CD_3OD): 80.6 (C-2), 42.4 (C-3), 198.5 (C-4), 167.0 (C-5), 98.1 (C-6), 164.6 (C-7), 96.9 (C-8), 164.0 (C-9), 116.4 (C-10), 130.9 (C-1), 129.1 (C-2, 6), 116.4 (C-3, 5), 159.1 (C-4), 101.3 (C-1), 74.7 (C-2), 78.3 (C-3), 71.2 (C-4), 77.9 (C-5), 62.4 (C-6).

Esculetin (**3**), $\text{C}_9\text{H}_6\text{O}_4$, yellow crystal, mp 285–286 (EtOH). ^1H NMR (400 MHz, DMSO): 6.11 (1H, d, $J=9.5$ Hz, H-3), 7.77 (d, $J=9.5$ Hz, H-4), 6.99 (1H, s, H-5), 6.76 (1H, s, H-8). ^{13}C NMR (125 MHz, DMSO): 161.5 (C-2), 112.5 (C-3), 144.7 (C-4), 112.9 (C-5), 143.9 (C-6), 151.4 (C-7), 103.4 (C-8), 149.8 (C-9), 111.8 (C-10). (Cussans N. J. *et al.* 1975).

Discussion

Seven known compounds which were isolated from *Ceratophyllum demersum* L. collected in Lijang County of Yunnan province, were compared them with the MeOH extracts of *Ceratophyllum demersum* L. collected in Kunming by TLC. The results shown that the compounds of main secondary metabolite from *Ceratophyllum demersum* L. collected in different place of Yunnan were very similar.

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